Structure of Fermionic Density Matrices: Complete N-Representability Conditions

David A. Mazziotti

Phys. Rev. Lett. **108**, 263002 — Published 27 June 2012

DOI: 10.1103/PhysRevLett.108.263002

Structure of Fermionic Density Matrices: Complete N-representability Conditions

David A. Mazziotti*
Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, IL 60637
(Dated: Submitted November 8, 2011; Resubmitted April 13, 2012)

We present a constructive solution to the N-representability problem—a full characterization of the conditions for constraining the two-electron reduced density matrix (2-RDM) to represent an N-electron density matrix. Previously known conditions, while rigorous, were incomplete. Here we derive a hierarchy of constraints built upon (i) the bipolar theorem and (ii) tensor decompositions of model Hamiltonians. Existing conditions D, Q, G, T1, and T2, known classical conditions, and new conditions appear naturally. Subsets of the conditions are amenable to polynomial-time computations of strongly correlated systems.

PACS numbers: 31.10.+z

The wavefunction of a many-electron quantum system contains significantly more information than necessary for the calculation of energies and properties. In 1955 Mayer proposed in *Physical Review* computing the ground-state energy variationally as a functional of the two-electron reduced density matrix (2-RDM) which, unlike the wavefunction, scales polynomially with the number N of electrons [1–3]. However, the 2-electron density matrix must be constrained to represent a many-electron (or N-electron) density matrix (or wavefunction); otherwise, the minimized energy is unphysically below the ground-state energy for $N > 2$. Coleman called these constraints *N-representability conditions* [4], and the search for them became known as the N-representability problem [5, 7–11]. In 1995 the National Research Council ranked the N-representability problem as one of the top unsolved theoretical problems in chemical physics [12]. While progress was limited for many years, recent advances in theory and optimization [13–21] have enabled the application of the variational 2-RDM method to studying strong correlation in quantum phase transitions [22], quantum dots [23], polyaromatic hydrocarbons [24], firefly bioluminescence [25], and metal-to-insulator transitions [26].

Despite the recent computational results with 2-RDM methods, a complete set of N-representability conditions on the 2-RDM—not dependent upon higher-order RDMs—has remained unknown. While formal solutions of the N-representability problem were developed in the 1960s [5, 6], practically they required the N-electron density matrix [1, 2]. In this Letter we present a constructive solution of the N-representability problem that generates a complete set of N-representability conditions on the 2-RDM. The approach is applicable to generating the N-representability conditions on the p-RDM for any $p \leq N$. The conditions arise naturally as a hierarchy of constraints on the 2-RDM, which we label the $(2, q)$-positivity conditions, where the $(2, 2)$- and $(2, 3)$-positivity conditions correspond to the already known D, Q, G T1, and T2 conditions [4, 5, 8, 16]. The second number in $(2, q)$ corresponds to the higher q-RDM which serves as the starting point for the derivation of the condition.

A key advance in extending the $(2, q)$-positivity conditions for $q > 3$ is the use of tensor decompositions in the model Hamiltonians that expose the boundary of the N-representable 2-RDM set. The decompositions allow the terms in the model Hamiltonians to have no more than two-body interactions through the cancelation of all higher 3-to-q-body terms. A second important element is the recognition that when $q = r$ where r is the rank of the one-electron basis set the positivity conditions are complete. The hierarchy of conditions can be thought of as a collection of model Hamiltonians [10]. For example, the 'basic' (2,2)-positivity conditions are both necessary and sufficient constraints for computing the ground-state energies of pairing model Hamiltonians [2, 15], often employed in describing long-range order and superconductivity.

Consider a quantum system composed of N fermions. A matrix is a fermionic *density matrix* if and only if it is: (*i*) Hermitian, (*ii*) normalized (fixed trace), (*iii*) antisymmetric in the exchange of particles, and (*iv*) positive semidefinite. A matrix is *positive semidefinite* if and only if its eigenvalues are nonnegative. The p-particle reduced density matrix (p-RDM) can be obtained from the N-particle density matrix by integrating over all but the first p particles

$$ {}^pD = \int {}^ND \, d(p+1) \ldots dN \tag{1}$$

The set of ND is a convex set which we denote as P^N while the set ${}^pD$ is a convex set which we denote as P^p_N, the set of N-representable p-particle density matrices. A set is *convex* if and only if the convex combination of any two members of the set is also contained in the set

$$ w \, {}^ND_1 + (1 - w) \, {}^ND_2 \in P^N, \tag{2}$$

where $0 \leq w \leq 1$. The integration in Eq. (1) defines a linear mapping from P^N to P^p_N, which preserves its convexity.

The energy of a quantum system in a stationary state can be computed from the Hamiltonian traced against the state's density matrix. For a system of N fermions we have

$$E = \mathrm{Tr}(\hat{H}\,{}^{N}D). \tag{3}$$

If the Hamiltonian is a p-body operator, meaning that it has at most p-particle interactions, then the energy can be written as a functional of only the p-RDM

$$E = \mathrm{Tr}(\hat{H}\,{}^{p}D). \tag{4}$$

For a system of N electrons the Hamiltonian generally has at most pairwise interactions, and hence, the energy can be expressed as a linear functional of the 2-RDM. Except when $N = 2$, however, minimizing the energy as a functional of a two-electron density matrix ${}^{2}D \in P^2$ yields an energy that is much too low. To obtain the correct ground-state energy, we must constrain the two-electron density matrix to be N-representable, that is ${}^{2}D \in P^2_N$.

Based on the equivalence of the energy expectation values in Eqs. (3) and (4), we can use the set P^p_N of N-representable p-particle density matrices to define a set ${P^p_N}^*$ of p-particle (Hamiltonian) operators ${}^{p}\hat{O}$ that are positive semidefinite in their trace with any N-particle density matrix

$${P^p_N}^* = \{{}^{p}\hat{O} | \mathrm{Tr}({}^{p}\hat{O}\,{}^{p}D) \geq 0 \text{ for all } {}^{p}D \in P^p_N\}. \tag{5}$$

The set ${P^p_N}^*$ is said to be the *polar* (or dual) of the set P^p_N. Importantly, by the *bipolar theorem* [6, 27], the set ${P^p_N}^*$ also fully defines its polar set P^p_N as follows

$$P^p_N = \{{}^{p}D | \mathrm{Tr}({}^{p}\hat{O}\,{}^{p}D) \geq 0 \text{ for all } {}^{p}\hat{O} \in {P^p_N}^*\}. \tag{6}$$

By Eq. (6) we have a complete characterization of the N-representable p-RDMs from a knowledge of all operators ${}^{p}\hat{O} \in {P^p_N}^*$ [6]. This analysis shows formally that there exists a solution to the N-representability problem [5, 6], but it does not provide a mechanism for characterizing the set ${P^p_N}^*$.

To characterize ${P^p_N}^*$, we assume that the N-fermion quantum system has r orbitals and hence, $r - N$ holes. A convex set can be defined by the enumeration of its *extreme elements*, that is the elements (or members) that cannot be expressed by a convex combination of other elements [2, 27]. The definition of ${P^p_N}^*$ in Eq. (5) for $p \leq N$ can be extended in second quantization to include $p > N$

$${P^p_N}^* = \{{}^{p}\hat{O} | \mathrm{Tr}({}^{p}\hat{O}\,{}^{N}D) \geq 0 \text{ for all } {}^{N}D\} \tag{7}$$

with the ${}^{p}\hat{O}$ being polynomials in creation and annihilation operators of degree $2p$. Because in second quantization the value of N is defined in the density matrices ${}^{N}D$ rather than in the operators ${}^{p}\hat{O}$ [28], the set ${P^p_N}^*$ provides complete N-representability conditions on the p-RDM for any N between 2 and r. The extreme operators in the set ${P^r_N}^*$ can be written as Hermitian squares of operators [29]

$${}^{r}\hat{O}_i = {}^{r}\hat{C}_i\,{}^{r}\hat{C}_i^{\dagger}, \tag{8}$$

where the ${}^{r}\hat{C}_i$ are polynomials in the creation and annihilation operators of degree less than or equal to r (i.e., Eqs. (19) and (20)). Because any operator ${}^{p}\hat{C}$ with $p > r$ reduces to a polynomial of degree r in its operation on any ${}^{N}D$, the sets ${P^p_N}^*$ with $p > r$ do not contain additional information about the positivity of ${}^{N}D$. To establish this reduction, we rearrange terms in ${}^{p}\hat{C}$ of degree greater than r into a normal order with either more than N annihilation operators to the right of the creation operators or more than $r-N$ creation operators to the right of the annihilation operators; in either situation, the terms of degree greater than r vanish in their operation upon any ${}^{N}D$.

The operators ${}^{p}\hat{O}$ that constrain the p-RDM to be N-representable in Eq. (6) are also necessary to constrain the q-RDM to be N-representable where $q > p$; formally, each ${}^{p}\hat{O} \in {P^p_N}^*$ can be lifted by inserting the number operator to the $(q-p)$ power to form a ${}^{q}\hat{O} \in {P^q_N}^*$ [15]. Therefore, as illustrated in Fig. 1, we have the following set relations

$${P^2_N}^* \subseteq {P^3_N}^* \subseteq {P^p_N}^* ... \subseteq {P^r_N}^*. \tag{9}$$

Consequently, extreme operators ${}^{r}\hat{O}_i$ of ${P^r_N}^*$ can be combined convexly to produce all p-body operators ${}^{p}\hat{O} \in {P^p_N}^*$, and hence, the extreme points of ${P^p_N}^*$ can be characterized completely by the convex combination of the

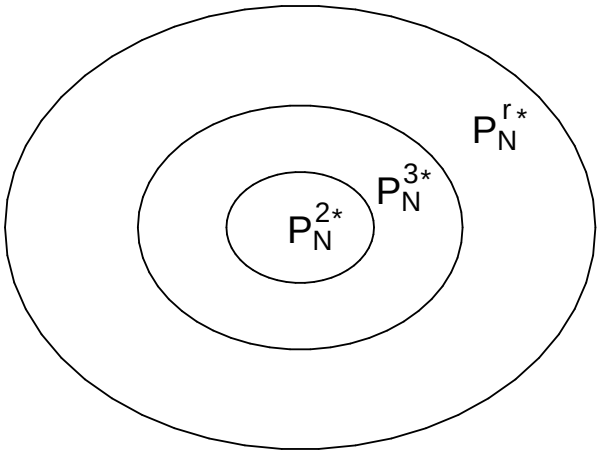

FIG. 1. The convex set ${P^2_N}^*$ of 2-body operators that are positive semidefinite in their trace with any N-particle density matrix is contained within the convex set ${P^3_N}^*$ of analogous 3-body operators, which in turn is contained within the set ${P^r_N}^*$. Hence, the extreme points of ${P^2_N}^*$ can be characterized completely by the convex combination of the extreme points of ${P^r_N}^*$, which are given by Eq. (8).

extreme points of ${P_N^r}^*$. More generally, convex combinations of extreme ${}^q\hat{O}_i \in {P_N^q}^*$ generate all p-body operators ${}^p\hat{O} \in {P_N^p}^*$ for $p < q$. Depending upon the order of the creation and annihilation operators in ${}^r\hat{O}_i$, the normal-ordered terms will have either positive or negative coefficients. Convex combinations of the ${}^r\hat{O}_i$ can be chosen to cancel the coefficients of all terms of degree greater than p. Extreme elements are generated from the minimum number of convex combinations to effect the cancelation. This characterization of the set ${P_N^p}^*$ provides a *constructive solution* of the N-representability problem for the p-RDM.

The constructive solution—convex combinations of the operators in Eq. (8)—generates the existing N-representability conditions as well as new conditions. The *(1,1)-positivity conditions* [4] are derivable from the subset of ${}^r\hat{C}_i$ operators in Eq. (8) of degree 1

$$\hat{C}_D = \sum_j b_j \hat{a}_j^\dagger \tag{10}$$

$$\hat{C}_Q = \sum_j b_j \hat{a}_j. \tag{11}$$

Keeping the trace of the corresponding one-body operators ${}^1\hat{O}_D$ and ${}^1\hat{O}_Q$ against the 1-RDM nonnegative for all values of b_j yields the conditions, ${}^1D \succeq 0$ and ${}^1Q \succeq 0$, where ${}^1D$ and ${}^1Q$ are matrix representations of the 1-particle and the 1-hole RDMs and the symbol $\succeq$ indicates that the matrix is constrained to be positive semidefinite.

Similarly, the *(2,2)-positivity conditions* [5] follow from considering the ${}^r\hat{C}_i$ operators of degree 2 in Eq. (8)

$$\hat{C}_D = \sum_{jk} b_{jk} \hat{a}_j^\dagger \hat{a}_k^\dagger \tag{12}$$

$$\hat{C}_Q = \sum_{jk} b_{jk} \hat{a}_j \hat{a}_k \tag{13}$$

$$\hat{C}_G = \sum_{jk} b_{jk} \hat{a}_j^\dagger \hat{a}_k. \tag{14}$$

Restricting the trace of the corresponding two-body operators ${}^2\hat{O}_D$, ${}^2\hat{O}_Q$, and ${}^2\hat{O}_G$ against the 2-RDM to be nonnegative for all values of $b_{j,k}$ defines the conditions, ${}^2D \succeq 0$, ${}^2Q \succeq 0$, and ${}^2G \succeq 0$, which constrain the probabilities for finding two particles, two holes, and a particle-hole pair to be nonnegative, respectively.

In general, the (q,q)-positivity conditions [13, 15] follow from restricting all q-body operators ${}^q\hat{O}$ in Eq. (8) to be nonnegative in their trace against the q-RDM [15]. While the (q,q)-positive operators are not two-body operators for $q > 2$, convex combinations of them generate two-body operators ${}^2\hat{O} \in {P_N^2}^*$ that enforce the N-representability of the 2-RDM. We refer to necessary N-representability conditions arising from convex combinations of (q,q)-positivity conditions as $(2,q)$-positivity conditions.

The simplest such constraints, the *(2,3)-positivity conditions*, arise from keeping the following convex combinations of 3-body operators in Eq. (8) nonnegative

$${}^2\hat{O}_{T1} = \hat{C}_{T1,1}\,\hat{C}_{T1,1}^\dagger + \hat{C}_{T1,2}\hat{C}_{T1,2}^\dagger \tag{15}$$

$${}^2\hat{O}_{T2} = \hat{C}_{T2,1}\,\hat{C}_{T2,1}^\dagger + \hat{C}_{T2,2}\hat{C}_{T2,2}^\dagger \tag{16}$$

where

$$\hat{C}_{T1,1} = \sum_{jkl} b_{jkl} \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_l^\dagger \tag{17}$$

$$\hat{C}_{T1,2} = \sum_{jkl} b_{jkl} \hat{a}_j \hat{a}_k \hat{a}_l \tag{18}$$

$$\hat{C}_{T2,1} = \sum_{jkl} b_{jkl} \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_l + \sum_j b_j \hat{a}_j^\dagger \tag{19}$$

$$\hat{C}_{T2,2} = \sum_{jkl} b_{jkl} \hat{a}_j \hat{a}_k \hat{a}_l^\dagger + \sum_j b_j \hat{a}_j. \tag{20}$$

These conditions, known as the $T1$ and generalized $T2$ conditions were developed by Erdahl [8] and implemented by Zhao *at al.* [16] and Mazziotti [15]. In general, they significantly improve the accuracy of the 2-positivity conditions.

Although the constructive proof given above indicates that a complete set of N-representability conditions can be generated from convex combinations of extreme elements of ${P_N^r}^*$, additional conditions have not been discovered beyond the (2,2)- and (2,3)-positivity conditions. For example, what about (2,4)-positivity conditions—that is, N-representability constraints on the 2-RDM arising from convex combinations of 4-body operators in Eq. (8)? First, we derive a class of (3,4)-positivity conditions on the 3-RDM.

Consider the nonnegativity of the following operator $\hat{O}$ formed by the convex combination of a pair of 4-body operators from Eq. (8)

$$\hat{O} = \hat{C}_{\mathrm{xxxx}}\,\hat{C}_{\mathrm{xxxx}}^\dagger + \hat{C}_{\mathrm{xooo}}\hat{C}_{\mathrm{xooo}}^\dagger \tag{21}$$

where the symbols x and o represent creation and annihilation operators, respectively, in the $\hat{C}$ operators defined as follows

$$\hat{C}_{\mathrm{xxxx}} = \sum_{jklm} b_{jklm} \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_m^\dagger \tag{22}$$

$$\hat{C}_{\mathrm{xooo}} = \sum_{jklm} d_{jklm} \hat{a}_j^\dagger \hat{a}_k \hat{a}_l \hat{a}_m. \tag{23}$$

Importantly, the expectation value of $\hat{O}$ with $d_{jklm} = b_{jklm}$ requires the 4-RDM because the cumulant part ${}^4\Delta$ of the 4-RDM [1, 30] does not vanish

$$\sum_{jklmpqst} b_{jklm} b_{pqst}^* \left({}^4\Delta_{pqst}^{jklm} - {}^4\Delta_{pklm}^{jqst}\right) \neq 0. \tag{24}$$

To obtain additional N-representability conditions requires that the dependence of the $\hat{C}$ operators on the expansion coefficients be *generalized from linear to nonlinear*. Specifically, to obtain 3-RDM conditions beyond the

TABLE I. A class of (2,4)-positivity conditions can be derived from convex combinations of the (4,4)-positivity conditions that cancel the 3- and 4-particle operators. We achieve the cancelation through tensor decomposition in the model Hamiltonians.

(2,4)-Positivity Conditions
$\mathrm{Tr}((3\hat{C}_{\mathrm{xxxx}}\hat{C}^{\dagger}_{\mathrm{xxxx}} + \hat{C}_{\mathrm{xxxo}}\hat{C}^{\dagger}_{\mathrm{xxxo}} + \hat{C}_{\mathrm{xxox}}\hat{C}^{\dagger}_{\mathrm{xxox}} + \hat{C}_{\mathrm{xoxx}}\hat{C}^{\dagger}_{\mathrm{xoxx}} + \hat{C}_{\mathrm{oxxx}}\hat{C}^{\dagger}_{\mathrm{oxxx}} + \hat{C}_{\mathrm{oooo}}\hat{C}^{\dagger}_{\mathrm{oooo}})^{2}D) \geq 0$
$\mathrm{Tr}((3\hat{C}_{\mathrm{xxxo}}\hat{C}^{\dagger}_{\mathrm{xxxo}} + \hat{C}_{\mathrm{xxxx}}\hat{C}^{\dagger}_{\mathrm{xxxx}} + \hat{C}_{\mathrm{xxoo}}\hat{C}^{\dagger}_{\mathrm{xxoo}} + \hat{C}_{\mathrm{xoxo}}\hat{C}^{\dagger}_{\mathrm{xoxo}} + \hat{C}_{\mathrm{oxxo}}\hat{C}^{\dagger}_{\mathrm{oxxo}} + \hat{C}_{\mathrm{ooox}}\hat{C}^{\dagger}_{\mathrm{ooox}})^{2}D) \geq 0$
$\mathrm{Tr}((3\hat{C}_{\mathrm{xxox}}\hat{C}^{\dagger}_{\mathrm{xxox}} + \hat{C}_{\mathrm{xxoo}}\hat{C}^{\dagger}_{\mathrm{xxoo}} + \hat{C}_{\mathrm{xxxx}}\hat{C}^{\dagger}_{\mathrm{xxxx}} + \hat{C}_{\mathrm{xoox}}\hat{C}^{\dagger}_{\mathrm{xoox}} + \hat{C}_{\mathrm{oxox}}\hat{C}^{\dagger}_{\mathrm{oxox}} + \hat{C}_{\mathrm{ooxo}}\hat{C}^{\dagger}_{\mathrm{ooxo}})^{2}D) \geq 0$
$\mathrm{Tr}((3\hat{C}_{\mathrm{xoxx}}\hat{C}^{\dagger}_{\mathrm{xoxx}} + \hat{C}_{\mathrm{xoxo}}\hat{C}^{\dagger}_{\mathrm{xoxo}} + \hat{C}_{\mathrm{xoox}}\hat{C}^{\dagger}_{\mathrm{xoox}} + \hat{C}_{\mathrm{xxxx}}\hat{C}^{\dagger}_{\mathrm{xxxx}} + \hat{C}_{\mathrm{ooxx}}\hat{C}^{\dagger}_{\mathrm{ooxx}} + \hat{C}_{\mathrm{oxoo}}\hat{C}^{\dagger}_{\mathrm{oxoo}})^{2}D) \geq 0$
$\mathrm{Tr}((3\hat{C}_{\mathrm{oxxx}}\hat{C}^{\dagger}_{\mathrm{oxxx}} + \hat{C}_{\mathrm{oxxo}}\hat{C}^{\dagger}_{\mathrm{oxxo}} + \hat{C}_{\mathrm{oxox}}\hat{C}^{\dagger}_{\mathrm{oxox}} + \hat{C}_{\mathrm{ooxx}}\hat{C}^{\dagger}_{\mathrm{ooxx}} + \hat{C}_{\mathrm{xxxx}}\hat{C}^{\dagger}_{\mathrm{xxxx}} + \hat{C}_{\mathrm{xooo}}\hat{C}^{\dagger}_{\mathrm{xooo}})^{2}D) \geq 0$
$\mathrm{Tr}((3\hat{C}_{\mathrm{xxoo}}\hat{C}^{\dagger}_{\mathrm{xxoo}} + \hat{C}_{\mathrm{xxox}}\hat{C}^{\dagger}_{\mathrm{xxox}} + \hat{C}_{\mathrm{xxxo}}\hat{C}^{\dagger}_{\mathrm{xxxo}} + \hat{C}_{\mathrm{xoxo}}\hat{C}^{\dagger}_{\mathrm{xoxo}} + \hat{C}_{\mathrm{oxoo}}\hat{C}^{\dagger}_{\mathrm{oxoo}} + \hat{C}_{\mathrm{ooxx}}\hat{C}^{\dagger}_{\mathrm{ooxx}})^{2}D) \geq 0$
$\mathrm{Tr}((3\hat{C}_{\mathrm{xoox}}\hat{C}^{\dagger}_{\mathrm{xoox}} + \hat{C}_{\mathrm{xooo}}\hat{C}^{\dagger}_{\mathrm{xooo}} + \hat{C}_{\mathrm{xoxx}}\hat{C}^{\dagger}_{\mathrm{xoxx}} + \hat{C}_{\mathrm{xxox}}\hat{C}^{\dagger}_{\mathrm{xxox}} + \hat{C}_{\mathrm{ooox}}\hat{C}^{\dagger}_{\mathrm{ooox}} + \hat{C}_{\mathrm{oxxo}}\hat{C}^{\dagger}_{\mathrm{oxxo}})^{2}D) \geq 0$
$\mathrm{Tr}((3\hat{C}_{\mathrm{xoxo}}\hat{C}^{\dagger}_{\mathrm{xoxo}} + \hat{C}_{\mathrm{xoxx}}\hat{C}^{\dagger}_{\mathrm{xoxx}} + \hat{C}_{\mathrm{xooo}}\hat{C}^{\dagger}_{\mathrm{xooo}} + \hat{C}_{\mathrm{xxxo}}\hat{C}^{\dagger}_{\mathrm{xxxo}} + \hat{C}_{\mathrm{ooxo}}\hat{C}^{\dagger}_{\mathrm{ooxo}} + \hat{C}_{\mathrm{oxox}}\hat{C}^{\dagger}_{\mathrm{oxox}})^{2}D) \geq 0$

(3,3)-positivity constraints, we must factor the 4-particle expansion coefficients b_{jklm} and d_{jklm} into products of 3- and 1-particle coefficients $b_j b_{klm}$ and $b_j b^*_{klm}$ which cause the cumulant part of the 4-RDM in $\langle\Psi|\hat{O}|\Psi\rangle$ to vanish

$$\sum_{jklmpqst} b_j b_{klm} b^*_p b^*_{qst} \, ({}^4\Delta^{jklm}_{pqst} - {}^4\,\Delta^{jklm}_{pqst}) = 0. \qquad (25)$$

The (3,4)-positivity condition, represented by Eq. (21) and the tensor decomposition of the expansion coefficients, is part of a class of (3,4)-conditions that arises from all distinct combinations of two 4-particle metric matrices that differ from each other in the replacement of *three* second-quantized operators by their adjoints.

A class of *(2,4)-positivity conditions*, shown in Table I, can be derived from convex combinations of the above (3,4)-positivity conditions that cancel the 3-particle operators, that is the products of six second-quantized operators. To effect the cancelation, the nonlinearity of the expansion coefficients of $\hat{C}$ must be increased from $b_j b_{klm}$ to $b_j c_k d_l e_m$. Specifically, the $\hat{C}$ operators in Table I are defined as

$$\hat{C}_{\mathrm{uvwz}} = \sum_{jklm} b^{\mathrm{u}}_j c^{\mathrm{v}}_k d^{\mathrm{w}}_l e^{\mathrm{z}}_m \hat{a}^{\mathrm{u}}_j \hat{a}^{\mathrm{v}}_k \hat{a}^{\mathrm{w}}_l \hat{a}^{\mathrm{z}}_m, \qquad (26)$$

where $\hat{a}^u_j$ and b^{u}_j are $\hat{a}^{\dagger}_j$ and b^*_j if u = x and $\hat{a}_j$ and b_j if u = o. Each of the eight (2,4)-positivity conditions in Table I generates an additional condition by switching all x's and o's in accordance with *particle-hole duality*, the symmetry between particles and holes. The (2,4)-conditions become the diagonal N-representability conditions [8, 31–33] when b, c, d, and e are restricted to be unit vectors; they are more general than the unitarily invariant diagonal conditions because these four vectors are not required to be orthogonal. These (2,4)-positivity conditions are only representative of the process by which complete conditions can be constructed from the solution of the N-representability problem presented in this Letter. Additional (2,4)-conditions in this class can be generated from reordering creation and annihilation operators in the conditions of Table I, and other extreme (2,4)-conditions can be constructed from lifting the (2,3)-conditions. A comprehensive list of (2,4)-positivity conditions as well as (2,3)-, (2,5)-, and (2,6)-positivity conditions, which are consistent with the constructive solution, will be presented elsewhere. The (2,5)- and (2,6)-conditions include extensions of three and eighteen classes of known diagonal conditions, respectively.

The set ${P^2_N}^*$ of N-representability conditions on the 2-RDM contains the set ${C^2_N}^*$ of *classical N-representability conditions* [8, 31–33], which ensure that the two-electron reduced density function (2-RDF), the diagonal (classical) part of the 2-RDM, can be represented by the integration of a N-particle density function. In different fields the set C^2_N of N-representable 2-RDF has been given different names: cut polytope [31] in combinatorial optimization and the correlation (or Boole) polytope [31, 35] in the study of 0-1 programming or Bell's inequalities. The set C^2_N, previously characterized, has important applications in global optimization including the search for the global energy minima of molecular clusters [33], the study of classical fluids [34], the max-cut problem in circuit design and spin glasses [31], lattice holes in the geometry of numbers, pair density (2-RDF) functional theory [32], and the investigation of generalized Bell's inequalities [35]. The characterization of the set P^2_N of N-representable 2-RDMs represents a significant generalization of the solution of the classical N-representability problem (the Boole 0-1 programming problem). In addition to its potentially significant applications to the study of correlation in many-fermion quantum systems, knowledge of the set P^2_N may have important applications to "quantum" analogues of problems in circuit design and the geometry of numbers.

The complete set of N-representability conditions firmly solidifies 2-RDM theory as a fundamental theory of many-body quantum mechanics with two-particle interactions. Rigorous lower bounds to the ground-state energy of strongly correlated quantum systems can be computed and improved in polynomial time from subsets of the complete N-representability conditions [21] (Minimizing the energy with a fully N-representable 2-RDM is a non-deterministic polynomial (NP) complete problem because $C^2_N \subset P^2_N$ with optimization in C^2_N

known to be NP-complete [31]). The present result raises challenges and opportunities for future research that include (i) implementing the higher N-representability conditions which are not in the form of traditional semidefinite programming [15, 16, 21], and (ii) determining which of the new conditions are most appropriate for different problems in many-particle chemistry and physics. Beyond their potential computational applications, the complete N-representability conditions for fermionic density matrices provide new fundamental insight into many-electron quantum mechanics including the identification and measurement of correlation and entanglement.

The author thanks D. Herschbach, H. Rabitz, and A. Mazziotti for encouragement, and the NSF, ARO, Microsoft Corporation, Dreyfus Foundation, and David-Lucile Packard Foundation for support.

* damazz@uchicago.edu

[1] *Two-electron Reduced-Density-Matrix Mechanics*, edited by D. A. Mazziotti, Advances in Chemical Physics Vol. 134 (Wiley, New York, 2007).

[2] A. J. Coleman and V. I. Yukalov, *Reduced Density Matrices: Coulson's Challenge* (Springer, New York 2000).

[3] J. E. Mayer, Phys. Rev. **100**, 1579 (1955).

[4] A. J. Coleman, Rev. Mod. Phys. **35** 668 (1963).

[5] C. Garrod and J. Percus, J. Math. Phys. **5**, 1756 (1964).

[6] H. Kummer, J. Math. Phys. **8**, 2063 (1967).

[7] J. E. Harriman, Phys. Rev. A **17**, 1257 (1978).

[8] R. M. Erdahl, Int. J. Quantum Chem. **13**, 697 (1978).

[9] R. M. Erdahl, Rep. Math. Phys. **15**, 147 (1979).

[10] J. K. Percus, Int. J. Quantum Chem. **13**, 89 (1978).

[11] M. Rosina, Adv. Chem. Phys. **134**, 11 (2007).

[12] F. H. Stillinger et al., *Mathematical Challenges from Theoretical/Computational Chemistry* (National Academic Press, Washington, D.C., 1995).

[13] R. M. Erdahl and B. Jin in *Many-electron Densities and Density Matrices*, edited by J. Cioslowski, (Kluwer, Boston, 2000).

[14] M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, J. Chem. Phys. **114**, 8282 (2001).

[15] D. A. Mazziotti, Phys. Rev. A **65**, 062511 (2002); Phys. Rev. Lett. **93**, 213001 (2004); Phys. Rev. A **74**, 032501 (2006).

[16] Z. Zhao, B. J. Braams, H. Fukuda, M. L. Overton, and J. K. Percus, J. Chem. Phys. **120**, 2095 (2004); M. Fukuda, B. J. Braams, M. Nakata, M. L. Overton, J. K. Percus, M. Yamashita, and Z. Zhao, Math. Program. Ser. B **109**, 553 (2007).

[17] E. Cancés, G. Stoltz, and M. Lewin, J. Chem. Phys. **125**, 064101 (2006).

[18] R. M. Erdahl, Adv. Chem. Phys. **134**, 61 (2007).

[19] B. Verstichel, H. van Aggelen, D. Van Neck, P. W. Ayers, and P. Bultinck, Phys. Rev. A **80**, 032508 (2009).

[20] N. Shenvi and A. F. Izmaylov, Phys. Rev. Lett. **105**, 213003 (2010).

[21] D. A. Mazziotti, Phys. Rev. Lett. **106**, 083001 (2011).

[22] G. Gidofalvi and D. A. Mazziotti, Phys. Rev. A **74**, 012501 (2006).

[23] A. E. Rothman and D. A. Mazziotti, Phys. Rev. A **78**, 032510 (2008).

[24] G. Gidofalvi and D. A. Mazziotti, J. Chem. Phys. **129**, 134108 (2008).

[25] L. Greenman and D. A. Mazziotti, J. Chem. Phys. **133**, 164110 (2010).

[26] A. Sinitskiy, L. Greenman, and D. A. Mazziotti, J. Chem. Phys. **133**, 014104 (2010).

[27] R. T. Rockafellar, *Convex Analysis* (Princeton University Press, Princeton, 1970).

[28] P. R. Surján, *Second Quantized Approach to Quantum Chemistry: An Elementary Introduction* (Springer-Verlag, New York, 1989).

[29] J. W. Helton, Ann. of Math. **156**, 675 (2002); J. W. Helton and S. McCullough, Trans. Amer. Math. Soc. **356**, 3721 (2004).

[30] D. A. Mazziotti, Chem. Phys. Lett. **289**, 419 (1998).

[31] M. M. Deza and M. Laurent, *Geometry of Cuts and Metrics* (Springer, New York, 1997).

[32] P. W. Ayers and E. R. Davidson, Adv. Chem. Phys. **134**, 443 (2007).

[33] E. Kamarchik and D. A. Mazziotti, Phys. Rev. Lett. **99**, 243002 (2007).

[34] J. Crawford, S. Torquato, and F. H. Stillinger, J. Chem. Phys. **119**, 7065 (2003).

[35] I. Pitowsky, Math. Program. **50**, 395 (1991).